REPORT 1158

PREDICTION OF FLAME VELOCITIES OF HYDROCARBON FLAMES [1]

By Gordon L. Dugger and Dorothy M. Simon

SUMMARY

The laminar-flame-velocity data previously reported by the Lewis laboratory are surveyed with respect to the correspondence between experimental flame velocities and values predicted by semitheoretical and empirical methods. The combustible mixture variables covered are hydrocarbon structure (56 hydrocarbons), equivalence ratio of fuel-air mixture, mole fraction of oxygen in the primary oxygen-nitrogen mixture (0.17 to 0.50), and initial mixture temperature (200° to 615° K). The semitheoretical methods of prediction considered are based on three approximate theoretical equations for flame velocity: the Semenov equation (bimolecular), which is primarily based on conductive heat transfer between the flame and the reactants; the Tanford-Pease equation, which is based on the diffusion of chain carriers of the oxidation reaction into the reactants; and the Manson equation, which is a modification of the momentum-pressure-drop equation that does not include chemical kinetics. In each equation a semiempirical factor is used to bring the predicted values for a given variable and fuel into the best average agreement with the data, so that the variation in the relative prediction of the individual datum points may be considered. For the resulting semitheoretical equations, it is assumed that thermal equilibrium is attained at the end of the flame zone, and values for the transport properties are estimated by extrapolation and simple additive relations. The empirical relations between combustible mixture variables and flame velocity are based on the usual methods of correlation.

Within these limitations, the results may be generalized as follows:

(1) The three semitheoretical equations predict relative flame velocities reasonably well, generally with mean deviations of 2 to 15 percent.

(2) Considering only the bimolecular fuel-oxygen reaction with low-temperature activation energies, the Semenov equation may be used to give good relative predictions when a "steric factor" is determined semiempirically.

(3) The average "specific rate constants" $\overline{k}_a$ obtained with the Tanford-Pease equation for molecular fuel—active particle reactions behave as Arrhenius rate constants only with the data on the effect of initial temperature, not with the equivalence-ratio or oxygen-concentration data. The relative predictions obtained by this equation are not very sensitive either to the temperature dependence assigned to the diffusion coefficients or to the recombination factor computed for hydrogen atoms. Regarding active particles considered, better results are generally obtained for hydrocarbon flames when the hydroxyl radical and the hydrogen and oxygen atoms (OH, H, and O) are considered rather then H alone; this is particularly true for studies of the effect of equivalence ratio.

(4) For the equivalence-ratio and oxygen-concentration data, considerably better relative predictions are obtained from the Manson equation when the pressure drop across the flame front is considered to be due to H, OH, and O than when only H atoms are taken into account.

(5) The example presented by the ethylene data shows that an empirically determined rate constant or proportionality factor from equivalence-ratio data at atmospheric pressure and room temperature may predict the effect of initial temperature or oxygen concentration within approximately 20 percent by the Semenov or Tanford-Pease equation and within approximately 30 percent by the Manson equation.

(6) For engineering applications, the effects of the parameters studied could be estimated just as satisfactorily, and more easily, by one or another of the empirical correlations indicated, as compared with the three semitheoretical equations considered. However, the use of the semitheoretical equations in some cases reduces the number of constants required.

INTRODUCTION

The ability to predict flame velocities of fuels is of growing importance in the field of aircraft propulsion, since a correlation has been found between the combustion efficiency of a ram-jet burner and the laminar flame velocity of the fuel (ref. 1). The prediction of flame velocities is difficult for three reasons: (1) There is no complete, rigorous theory which can be readily applied. There are, however, a number of approximate equations in the literature which approach the problem of flame propagation from various viewpoints. (2) There are no data on the kinetics of the oxidation process under flame conditions and very few data on transport

[1] Supersedes NACA RM E52J13, "Prediction of Flame Velocities of Hydrocarbon Flames," by Gordon L. Dugger and Dorothy M. Simon, 1952.

properties at high temperatures. (3) Different methods of flame-velocity measurement give different values; thus, it is difficult to compare data from different sources. The uncertainty in measurements made by a given method is of the order of 5 percent.

The present study and the calculations required for it were made during 1951–52. The study covers all the data obtained on the effects of hydrocarbon structure, initial temperature, and hydrocarbon-oxygen-nitrogen mixtures which were obtained at the NACA Lewis laboratory prior to September, 1952 (refs. 2 to 9). The semitheoretical methods are based on the Semenov equation (ref. 10), the Tanford-Pease square-root law (refs. 11 and 12), and the Manson equation (ref. 13). These three equations were derived from different models of the flame-propagation process. The Semenov model is essentially a thermal model which includes chemical reaction kinetics; the Tanford-Pease model is based on the diffusion of chain carriers of the oxidation reaction; and Manson used a modification of the momentum-pressure-drop equation which does not include chemical kinetics. The empirical relations for the effect on maximum flame speed of hydrocarbon structure, of initial mixture temperature, and of oxygen concentration were based on the usual methods of correlation.

It is recognized that there are other approximate theoretical equations which may give as good or better predictions of the NACA experimental results. The particular equations used were chosen because they exemplify three different approaches to the problem and because the Semenov and Tanford-Pease equations were used in previous NACA papers and many of the calculations had already been made individually. It is also recognized that there are many flame-speed data in the literature which could be used in such studies; the present paper is confined to NACA data because many of the calculations had been made, and because it was desirable to avoid the complications arising from comparing data obtained by many different methods and techniques.

NOMENCLATURE

The following nomenclature is used in this paper:

a	fuel concentration, molecules of fuel per cm³ of mixture
b	oxygen concentration, molecules of oxygen per cm³ of mixture
B_i	term near unity arising from radical recombination
C_p	molar heat capacity at constant pressure, cal/(mole) (°K)
c_p	specific heat, cal/(g) (°K)
$\overline{c}_p$	mean specific heat, T_0 to T_f, cal/(g) (°K)
D	diffusion coefficient, cm²/sec
D_i	diffusion coefficient of ith active species into unburned gas, cm²/sec
E	activation energy, kcal/g-mole
$\overline{E}_a$	fitted activation energy for group of data points, kcal/g-mole
K	empirical proportionality constant between experimental flame velocity and value predicted by Manson equation
K_H	empirical K from Manson equation when $\Delta p=1/2 p_H \frac{T_0}{T_f}$
K_Σ	empirical K from Manson equation when $\Delta P=1/2\left(p_H+p_{OH}\frac{D_{OH}}{D_H}+p_O\frac{D_O}{D_H}\right)\frac{T_0}{T_f}$
$\overline{K}_H,\overline{K}_\Sigma$	average K_H or K_Σ for group of data points
k	specific rate constant, cm³/(molecule) (sec)
k_a	weighted mean k_i for the three active particles H, OH, and O, each reacting with fuel molecules, cm³/(molecule) (sec)
$\overline{k}_a$	average k_a for group of data points, cm³/(molecule) (sec)
k_i	specific rate constant for reaction between fuel molecule and ith active particle, cm³/(molecule) (sec)
$\overline{k}_i$	average k_i for group of data points, cm³/(molecule) (sec)
L_m	total concentration of gas at mean combustion-zone temperature, molecules/cm³
M	molecular weight
n	total number of molecules of H_2O and CO_2 in products per molecule of fuel by stoichiometric relation
n_1/n_2	moles of reactants per mole of products from stoichiometric equation
P	steric factor, or probability factor, from the expression $k=PZ\exp[-E/RT]$
$\overline{P}$	average P for group of data points
p	total pressure of mixture
p_i	mole fraction of ith active particle in burned gas (equilibrium flame temperature)
Q	mole fraction of potential combustion product in unburned gas
Q'	mole fraction of fuel in unburned gas
R	universal gas constant, kcal/(g-mole) (°K) or ergs/(g-mole) (°K)
r	exponent showing molecularity of flame reaction
T	absolute temperature, °K
U	flame velocity, cm/sec; implies maximum flame velocity with respect to equivalence ratio, except in discussion of variation of equivalence ratio
w	reaction rate, molecules reacting per cm³/sec
x_j	mole fraction of jth component
Z	collision number; number of molecular collisions per second when concentration is one molecule of each type per cm³
α	mole fraction of oxygen in oxygen-nitrogen portion of mixture, $O_2/(O_2+N_2)$
δ	percentage mean deviation in ratio of predicted flame velocity to experimental value for given group of data
η	viscosity of mixture, poise
η_j	viscosity of jth component, poise
θ_m	ratio of mean reaction-zone temperature to initial temperature
λ	thermal conductivity, cal/(cm²) (sec) (°K/cm)
ρ	density of mixture, g/cm³

σ collision diameter, cm

φ equivalence ratio, fraction of stoichiometric fuel-oxygen ratio

Subscripts:

a average value for the three active particles (H, OH, and O)

eff effective value at mean reaction temperature

f conditions at computed equilibrium flame temperature

j any component of reaction products

m conditions at mean reaction-zone temperature

0 initial conditions

APPROXIMATE THEORETICAL EQUATIONS USED

SEMENOV BIMOLECULAR EQUATION

Zeldovich and Frank-Kamenetsky obtained an approximate solution for the rate of flame propagation from the differential equations for heat conduction and fuel concentration change across the flame front. This approximate solution was presented in detail by Semenov (ref. 10). The general approximate solution may be written (see ref. 10, pp. 31, 48, and 49):

$$U=\sqrt{\frac{2\lambda\int_0^{T_f} w\,dT}{a_0\rho_0\bar{c}_p(T_f-T_0)}\left(\frac{n_1}{n_2}\right)^r\left(\frac{\lambda}{Dc_p\rho}\right)_f^r} \tag{1}$$

where, for a bimolecular reaction between unlike molecules $r=2$ and

$$\int_0^{T_f} w\,dT=\int_0^{T_f} k(a)(b)\,dT$$

$$=a_{eff}\,b_{eff}PZ\frac{RT_f^2}{E}\exp\left(-E/RT_f\right) \tag{2}$$

For lean mixtures, $\varphi<1$, a_{eff} and b_{eff} are computed by (following the assumptions of ref. 10, p. 45):

$$a_{eff}=a_0\frac{T_0}{T_f}\frac{RT_f^2/E}{T_f-T_0} \tag{3a}$$

$$b_{eff}=b_0\frac{T_0}{T_f}\left[1-\varphi\left(1-\frac{RT_f^2/E}{T_f-T_0}\right)\right] \tag{3b}$$

For rich mixtures, $\varphi>1$:

$$a_{eff}=a_0\frac{T_0}{T_f}\left[1-\frac{1}{\varphi}\left(1-\frac{RT_f^2/E}{T_f-T_0}\right)\right] \tag{4a}$$

$$b_{eff}=b_0\frac{T_0}{T_f}\frac{RT_f^2/E}{T_f-T_0} \tag{4b}$$

For stoichiometric mixtures, equations (3) and (4) are identical. All of the factors in equations (1) through (4) can, with the exceptions of P and E, be estimated by the extrapolation of thermodynamic tables (refs. 14 and 15) or calculated by the relations

$$\eta=\sum \eta_j x_j \tag{5a}$$

(Values of η calculated for combustion-product mixtures by equation (5a) were within 1 percent of values calculated by the method of ref. 16.)

$$C_p=\sum_j C_{p,j}x_j \tag{5b}$$

$$\lambda=\left(C_p+\frac{5}{4}R\right)\frac{\eta}{M}\ \text{(ref. 15)} \tag{5c}$$

$$D=1.336\,\frac{\eta}{\rho}\ \text{(ref. 17)} \tag{5d}$$

$$\rho=\frac{pM}{RT} \tag{5e}$$

$$Z=\left(\frac{\sigma_1+\sigma_2}{2}\right)^2\left[8\pi RT\,\frac{(M_1+M_2)}{M_1M_2}\right]^{1/2} \tag{5f}$$

Flame-velocity predictions by the Semenov equation are evaluated herein as follows. Activation energies from low-temperature reactions and measured flame velocities are substituted in equation (1) and a steric factor P is calculated for each experimental flame velocity. These P's are then averaged to give $\bar{P}$ for the group of data points. The ratio of the predicted flame velocity to the experimental velocity is calculated as $(\bar{P}/P)^{1/2}$. The average deviation of the ratios from 1 is considered to be a measure of the accuracy of the predicted flame velocities. (The word accuracy is used to denote the degree of correspondence between flame velocities calculated by the methods described and measured flame velocities.)

The data for various hydrocarbons consisted of maximum flame velocities (maximum with respect to equivalence ratio) of 56 pure hydrocarbons at 298° K and atmospheric pressure (refs. 2 and 3). These data were obtained by the NACA tube method. The hydrocarbons included straight and branched chain members of the alkane, alkene, alkadiene, alkyne, and cycloalkane series and benzene. No calculations are made by the Semenov equation for these data, because the work required by this treatment would not be warranted in view of the slight differences in flame velocities observed for most of the hydrocarbons studied. However, it has been shown by more approximate calculations (ref. 18) that relative predictions would be satisfactory. Examples of these calculated values are given in table I.

The initial-mixture-temperature data included maximum flame velocities of methane-air, propane-air, and ethylene-air mixtures obtained by a Bunsen burner method (total-area method, outside edge of shadow cast by flame cone, ref. 5) at seven initial mixture temperatures ranging from 200° to 617° K. The following activation energies, in kilocalories per gram-mole, are reported in references 19, 20, and 21, respectively: methane, 51; propane, 38; ethylene, 40. These values are used in the Semenov equation to evaluate the flame-velocity predictions

TABLE I.—EXAMPLES OF PREDICTED MAXIMUM FLAME VELOCITIES FOR VARIOUS HYDROCARBON-AIR MIXTURES AT ROOM CONDITIONS

Hydrocarbon	Flame velocity, cm/sec		
	Measured (ref. 3)	Calculated by simplified Semenov equation (ref. 18)	Calculated by Tanford-Pease equation using $\bar{k}_a$ (ref. 25)
Methane	33.8	40.2	33.9
Propane	39.0	39.0	37.7
Hexane	38.5	37.2	37.3
2-Methylbutane	36.6	38.8	37.1
2,3-Dimethylbutane	36.3	39.1	37.0
2,2,3-Trimethylbutane	35.9	37.0	36.6
Propylene	43.8	48.9	45.3
Hexene-1	42.1	42.0	41.7
2-Ethylbutene-1	39.3	41.7	40.7
Propyne	69.9	64.9	61.3
Hexyne-1	48.5	46.0	48.6
Cyclohexane	38.7	38.3	37.4
Benzene	40.7	44.5	40.4

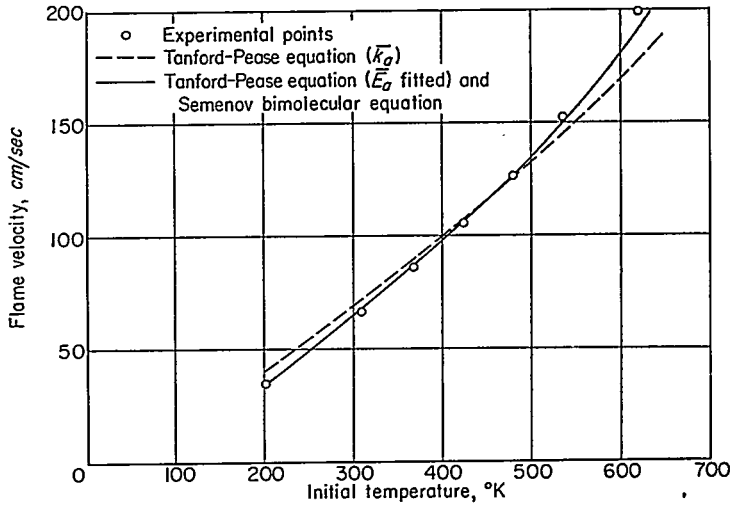
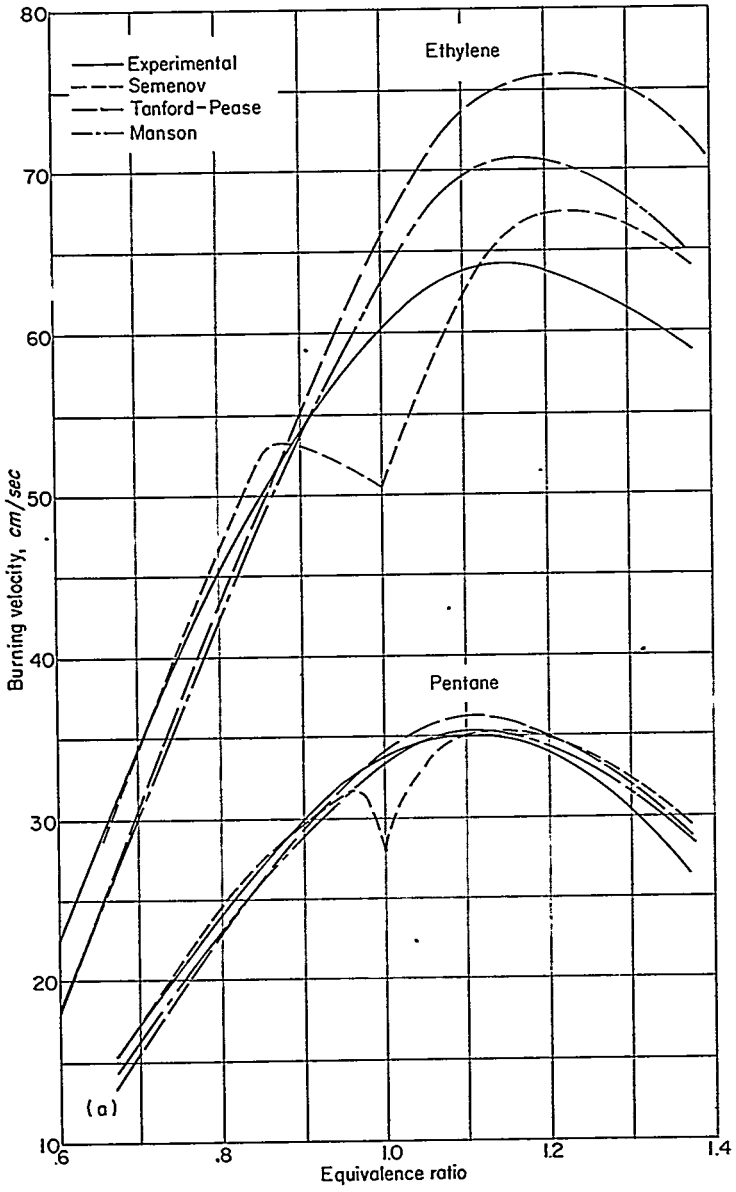
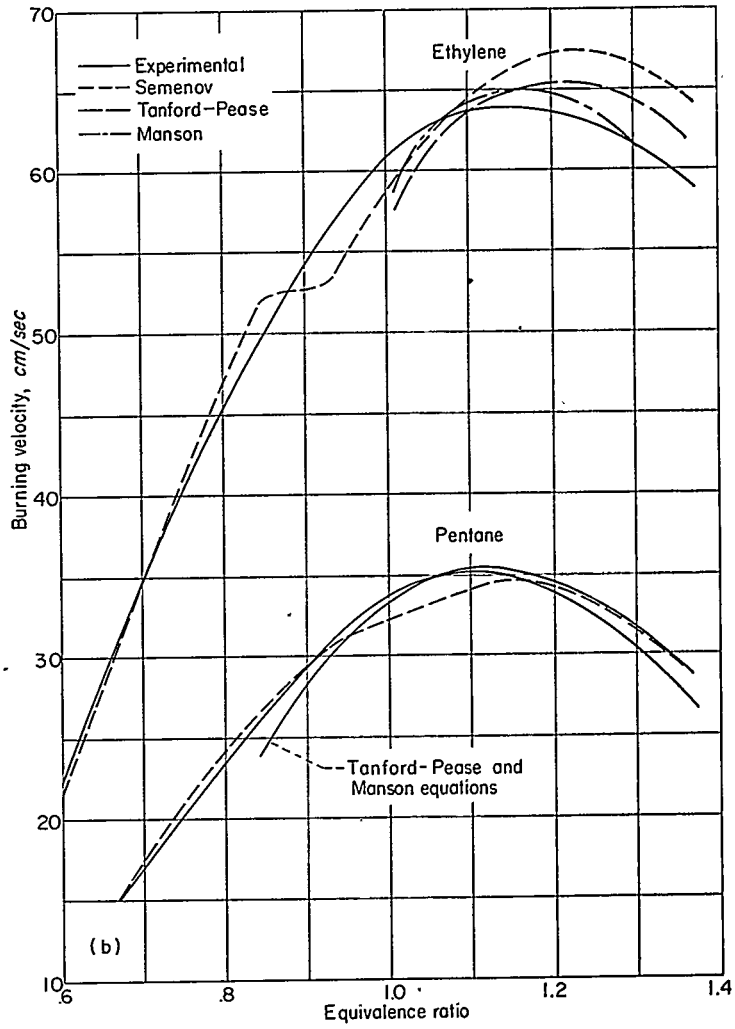


FIGURE 1.—Comparison of measured and calculated burning velocities for ethylene-air mixtures at different initial temperatures.



(a) Complete experimental range.



(b) Limited range.

FIGURE 2.—Predictions of effect of equivalence ratio on flame velocity

TABLE II.—PERCENTAGE MEAN DEVIATIONS IN RATIO OF PREDICTED TO MEASURED FLAME VELOCITY

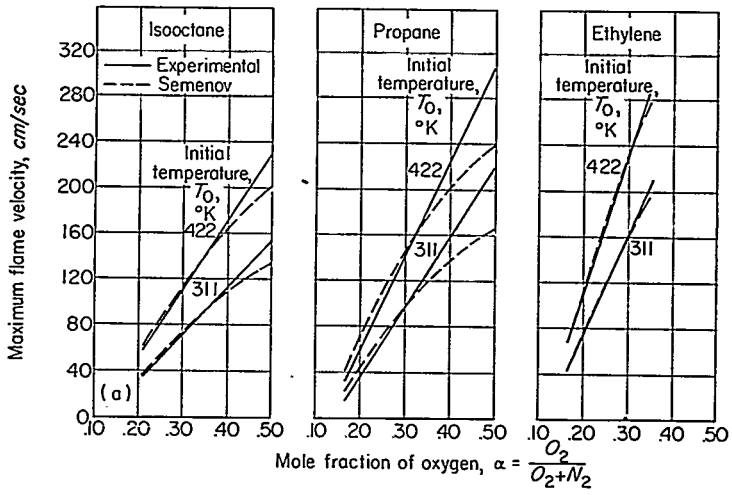
Type of data	Derivation of empirical correlation, percent		Deviations of semitheoretical predictions, percent					
	Form of correlation	Deviation	Semenov bimolecular equation	Tanford-Pease equation			Manson equation	
				Using $\bar{k}_H$	Using $\bar{k}_a$	Using $\bar{k}$ from T_0 data	Using $\bar{K}_B$	Using $\bar{K}_\Sigma$
Hydrocarbon structure [a]	$U=N_AK_A+N_BK_B+\ldots$	1.9		3.3	3.5		3.6	3.8
Initial temperature [b] (200° to 615° K)	$U=a+bT_0^n$							
Methane		2.1	2.7	11.8	7.8	0.8	10.3	10.1
Propane		1.6	2.0	12.5	6.1		10.0	13.0
Ethylene		1.4	1.8	9.4	5.8	1.8	12.0	13.8
Equivalence ratio (range limited, see text)	$U=a(\log B)+b$							
Methane, 307° K [b]			7.4	25.8	5.7	7.0	23.6	1.8
Pentane [a]		4.9	3.0	64.8	3.8		39.9	3.6
Propane, 302° K [b]			4.0		0.6		15.1	1.2
Ethylene [a]		2.2	5.0	16.6	3.7	3.3	10.0	1.8
Oxygen concentration [c]								
Propane, 311° K	$U=aT_0^n(\alpha-b)$	5.5	17.3		6.4		16.5	15.2
422° K			12.4		5.2		12.7	13.0
Ethylene, 311° K	$U=aT_0^n(\alpha-b)$	3.2	4.0		4.9		7.5	5.2
422° K			3.0		4.6		6.8	5.3
2,2,4-Trimethylpentane, 311° K	$U=a(\alpha-b)$	2.0	6.4		4.5		7.3	1.1
422° K		2.7	7.3		4.0		8.2	1.1
	$U=aT_0^n(\alpha-b)$	2.6						

[a] Data determined by tube method at room temperature (refs. 2 to 4).
[b] Data determined by Bunsen burner method, shadow cone (ref. 5).
[c] Data determined by Bunsen burner method, schlieren cone (refs. 6 and 7).

An example of these relative predictions is presented for ethylene-air mixtures in figure 1. Using the average steric factor $\bar{P}$ for this group of data and the aforementioned activation energy results in perfect agreement between the middle portion of the curve predicted by the Semenov bimolecular equation and the experimental points. The predicted curve diverges slightly from the experimental points at higher or lower flame velocities so that the mean deviation for the whole range is 1.8 percent. The average deviations obtained for the three fuels are tabulated in table II under "Semenov equations." It may be noted that essentially the same average deviations would result from the curves in reference 5 although the calculations were made by a more approximate method and the predicted flame velocities were referred to the experimental value for 25° C.

Two kinds of mixture-composition variables are studied. The first is the change of hydrocarbon concentration in air over an equivalence-ratio range of 0.7 to 1.3. Flame-velocity values by the tube method for ethylene-air and pentane-air mixtures at 298° K (ref. 4) and Bunsen-burner values (total-area method, outer edge of cone shadow) for methane-air mixtures at 307° K and propane-air mixtures at 302° K (ref. 5) are used. When the effect of changes in equivalence ratio on the flame velocity is computed by the Semenov equation, it is found that the approximations used in equations (3) and (4) are not consistent for the region near stoichiometric, particularly for equivalence ratios between 0.95 and 1.05. This fact is shown by the difference between the Semenov curves in figure 2 (a), where points in the range 0.95 to 1.05 are included in plotting the curve, and figure 2 (b), where these points are omitted. If this critical region is omitted, the accuracy of the predicted flame velocities over the equivalence range is 3 to 7 percent. Specific deviations are listed in table II.

The second composition variable studied is the ratio of oxygen to oxygen plus nitrogen $\alpha=O_2/(O_2+N_2)$. Maximum flame velocities (Bunsen-burner total-area method, outside edge of schlieren cone, refs. 6 and 7) for several α ratios were available for the following fuels and ranges of α: propane, 0.17 to 0.50; ethylene, 0.17 to 0.35; and 2,2,4-trimethylpentane, 0.21 to 0.50. The predicted curves from references 6 and 7 are reproduced in figure 3 (a). As in the initial-temperature example in figure 1, the predicted curves cross the experimental curve near the middle of the flame-velocity range. The accuracy of prediction of these data is 3 to 17 percent (table II).



(a) Semenov bimolecular equation (thermal mechanism).

FIGURE 3.—Effect of oxygen concentration on maximum flame velocities. Comparison of theoretically predicted curves with experimental results.

It may be noted in table II that flame-velocity predictions, by the Semenov equation for ethylene flames are accurate to 5 percent for variations in both composition and initial temperature. For these predictions (as discussed previously), each type of data was considered separately, and steric factors were calculated from the data. Now usually, when it is desired to predict flame velocities, only one type of data is available—for example, fuel-air-ratio data at atmospheric pressure and room temperature. It is therefore important to know how well the effects of initial temperature and oxygen concentration can be predicted from such data. The ethylene data are used in the following example.

The steric factor $\overline{P}$ calculated from the equivalence-ratio data and the low-temperature activation energy of 40 kilocalories per gram-mole are used in the Semenov equation to predict flame velocities over the ranges of initial temperature and oxygen concentration covered by the experimental data. In both cases the predicted flame velocities deviate from the normalized, measured flame velocities by an average of +14 percent, the maximum deviation being +24 percent for the oxygen-concentration data. (Because different methods of measuring flame velocity were used, differences in values for mixtures of the same composition and temperature were found. For these calculations all flame velocities are normalized by a simple ratio factor to the values for the initial-temperature data.)

TANFORD-PEASE EQUATION

Tanford and Pease (refs. 11, 12, and 22) equated the amount of product formed in the combustion zone by a second-order reaction between fuel molecules and hydrogen atoms (or other active particles such as hydroxyl radicals or oxygen atoms) to the amount of product formed at the flame front by conversion of the fresh gas expressed in terms of initial conditions and flame velocity. An approximate solution for flame velocity from this equation was given:

$$U=\left(\frac{L_m Q' n}{Q\theta_m{}^2}\sum_i \frac{k_i p_i D_{i,m}}{B_i}\right)^{1/2} \tag{6}$$

Three methods of evaluating the predictions of the Tanford and Pease equation are used herein. For all three, the following calculations are the same: (a) Flame temperature T_f and active particle concentrations p_i are calculated assuming adiabatic thermal equilibrium by a matrix method (ref. 23); (b) the mean combustion-zone temperature is assumed to be 0.7 T_f (ref. 11); (c) diffusion coefficients $D_{i,m}$ are calculated from $D_{i,m}=D_{i,0}\ (0.7\ T_f/T_0)^{1.67}$, where $D_{i,0}$ is the diffusion coefficient at initial temperature calculated by the Stefan-Maxwell equation (ref. 24); (d) the recombination factor B_i is calculated by the method of Tanford (ref. 12) for the hydrogen atoms and is assumed to be 1 for OH and O; (e) the ratio $L_m Q' n/Q$ is calculated from a knowledge of the over-all oxidation process and the initial concentration of reactants.

The three methods of evaluation differ in the calculation of k_i. For the first method only one chain carrier, the hydrogen atom, is considered. For this case k_H values are calculated from single-point flame-velocity determinations by equation (6). For the second method, H, O, and OH are considered to be the chain carriers and

$$\sum_i \frac{k_i p_i D_{i,m}}{B_i}\cong k_a\left(\frac{p_H D_{H,0}}{B_H}+p_{OH}D_{OH,0}+p_O D_{O,0}\right)\left(\frac{0.7\,T_f}{T_0}\right)^{1.67} \tag{7}$$

Single-point k_a values are calculated. For these two methods, the ratios of the predicted flame velocity to the experimental flame velocity is calculated as $(\overline{k}_H/k_H)^{1/2}$ and $(\overline{k}_a/k_a)^{1/2}$, respectively, and the average deviations of the ratios from 1 are used as a measure of the accuracies of the predictions.

For the third method, an Arrhenius type temperature dependence of the rate constant is used:

$$k_a=P_a Z_a \exp\left[-E_a/R(0.7\ T_f)\right] \tag{8}$$

The following method is used to calculate an activation energy $\overline{E}_a$ for best fit from the initial-temperature data. Several values of E_a are substituted in the equation and for each a value of $(\overline{P}/P)^{1/2}$ is calculated. Then δ, the percentage mean deviation in $(\overline{P}/P)^{1/2}$ for the group, is plotted against the E_a used. The "fitted" value of $\overline{E}_a$ is the one which gives the minimum δ. All other calculations by the third method are made by use of equations (7) and (8), measured flame velocities, and $\overline{E}_a$ from initial-temperature data. The accuracy is calculated as the mean deviation of $(\overline{P}/P)^{1/2}$ from 1.

The predictions of the Tanford-Pease equation are evaluated by methods 1 and 2 for the maximum flame velocities of a series of hydrocarbons (ref. 25). Examples of the predictions based on $\overline{k}_a$ are shown in table I. Table II shows that the mean deviation for 55 hydrocarbons (excluding ethylene) is 3.3 percent considering hydrogen atoms $\overline{k}_H$ only, and 3.5 percent considering all three active particles $\overline{k}_a$. These mean deviations are small enough to indicate either that the "rate constants" are not temperature-dependent, in which case the steric factors are of the order of 10^{-3}, or that $\exp\left[\overline{E}_a/R(0.7T_f)\right]\sqrt{T_f}$ is nearly constant for the hydrocarbons studied, which is probable. If the activation energy is of the order of 10 kilocalories per gram-mole, the steric factor is of the order of 10^{-2}.

All three methods of evaluation are used with the initial-temperature data. The accuracy of the flame velocity predictions is 9 to 12 percent (table II) for the first method $(\overline{k}_H)$ and 6 to 8 percent for the second method. The curves predicted for ethylene by use of methods 2 and 3 are shown in figure 1. The use of method 3, which includes the temperature dependence of the rate constant, improves the prediction so that the accuracy is about 2 percent. The calculated activation energies and steric factors are: for methane, 17 and 0.19; and for ethylene, 18 and 0.21. The calculated activation energy for ethylene is high when compared with the experimental activation energy for the reaction $H + C_2H_4 \rightarrow C_2H_5$, which is 2.6 kilocalories (calculated from data in ref. 26). The relative predictions are not appreciably changed by assuming $B_H=1$ or by assuming $D_{i,m}\propto T_m{}^2$ which was used in reference 7 instead of $D_{i,m}\propto \eta/\rho$.

If the entire range of equivalence ratios which was covered experimentally by the flame-velocity data is used for the prediction of velocities by the Tanford-Pease method, the accuracy of prediction is very poor as illustrated in figure 2 (a) for ethylene. If the equivalence ratios are limited to a small range near the ratio for the maximum flame velocity (for example, $\varphi=\varphi_{max}\pm0.15$), the accuracy of the predictions is 1 to 6 percent (table I) when all active particles are considered. However, if only hydrogen atoms are used the accuracy is very poor—17 to 65 percent.

The variations of flame velocity with oxygen concentration are calculated for all active particles. The accuracy of prediction is 4 to 6 percent. The predicted curves are shown in figure 3 (b).

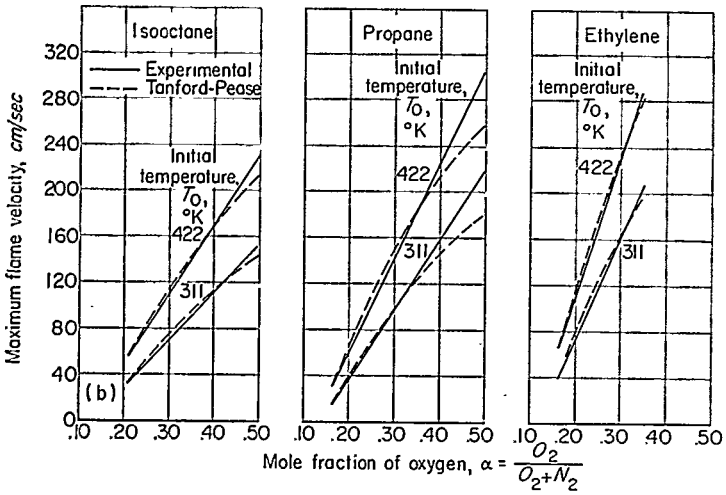
The ethylene data are again used as an example to show how well an average "rate constant" ($\overline{k}_a$ from method 2) from the fuel-air-ratio data predicts the effects of temperature and oxygen concentration on the maximum flame velocity. Predicted flame velocities for various temperatures differ from the normalized experimental values by −9 to +13 percent with an average deviation of 6 percent. Predicted flame velocities for various oxygen concentrations differ from experimental values by +8 to +22 percent with an average deviation of 12 percent.

MANSON EQUATION

The momentum relation between the flame (or combustion wave) velocity and the pressure drop across a plane, steady-state flame front, may be expressed in the form (ref. 27):

$$U=\left(\frac{\rho_f}{\rho_0}\frac{\Delta p}{\rho_0-\rho_f}\right)^{1/2} \tag{9}$$

Manson (ref. 13) suggested that the small pressure drop could be caused by the projection of hydrogen atoms into the unburned gas. Because the H atoms would recombine to H_2 at the unburned gas temperature, Δp was assumed to be one-half the equilibrium H atom pressure reduced to unburned gas temperature. In the present paper, Δp is calculated as both $\frac{1}{2}p_H\frac{T_0}{T_f}$ and $\frac{1}{2}\left(p_H+p_{OH}\frac{D_{OH,o}}{D_H}+p_O\frac{D_{O,o}}{D_H}\right)\frac{T_0}{T_f}$. The second method of calculating Δp takes into account three of the lightest and most abundant species which might be considered active particles and assumes that all of these would recombine in pairs. The average proportionality factor for a group of data is calculated by dividing the experimental flame velocity by the right side of equation (9) for each point and averaging the quotients. These average empirical proportionality factors are designated $\overline{K}_H$ for the first method and $\overline{K}_\Sigma$ for the second. The accuracy of the predicted flame velocities is considered to be the average deviation of $\overline{K}_H/K_H$ or $\overline{K}_\Sigma/K_\Sigma$ from 1. For the maximum flame velocities of the different hydrocarbons, the accuracy of prediction by the Manson equation for either method of evaluation is about 4 percent (table II). For the first method ($\overline{K}_H$), the proportionality factor is 0.5; that is, the predicted value is twice the experimental value.



(b) Tanford and Pease square-root law (diffusion mechanism).

FIGURE 3.—Concluded. Effect of oxygen concentration on maximum flame velocities. Comparison of theoretically predicted curves with experimental results.

For the initial-temperature data, the predicted flame velocities differ from the experimental velocities by 10 to 14 percent. When the total range of the equivalence-ratio data is considered, the accuracy of prediction of flame velocities by the Manson equation and either of the methods of evaluating Δp is poor. If the equivalence range is limited as for the Tanford-Pease method and with all active particles, predictions accurate to 2 to 4 percent are obtained (table II). The accuracy of prediction of flame velocities for mixtures containing different concentrations of oxygen varies from hydrocarbon to hydrocarbon. For 2,2,4-trimethylpentane, the accuracy is about 1 percent; for ethylene, 5 percent; and for propane, 15 percent.

The ethylene data are again considered in order to determine the accuracy with which the $\overline{K}_\Sigma$ from the equivalence-ratio data predicts the effects of temperature and oxygen concentration on flame velocity. The deviations for the initial-temperature data varied from −8 to +45 percent with a mean deviation of 27 percent. For the oxygen data the deviations varied from +1 to +19 percent with a mean value of +10 percent.

EMPIRICAL CORRELATIONS

A correlation was obtained (ref. 28) by which maximum flame velocities of various hydrocarbons in air could be predicted with an average deviation of 2 percent. The predicted flame velocity is calculated from the sum of the contributions of various H—C bonds in the fuel molecule according to the following relation:

$$U=N_AK_A+N_BK_B+N_CK_C+\ \ldots$$

where N_A, N_B, N_C, N_D, N_E, N_F, N_G, and N_H are the numbers of methane, primary, secondary, tertiary, alkene, alkyne, cyclohexyl, and aromatic C—H bonds, respectively, per unit volume of hydrocarbon-air mixture, and K_A, K_B, K_C, . . . are the flame-speed coefficients of these bonds. For the special cases of C—H bonds on carbon atoms placed alpha to alkyne C≡C bonds, a factor $M=0.96$ was introduced into terms representing these alpha bonds. Correlation coefficients (table III) established from 34 hydrocarbons

excluding ethylene then gave an average deviation of 1.9 percent in the ratio of predicted to measured flame velocity.

A correlation was also observed between the equivalence ratio for maximum flame velocity and the total bond dissociation energy of the fuel. As shown in table IV, the total bond dissociation energy per unit volume of the hydrocarbon-air mixture corresponding to the maximum flame velocity is nearly constant, with an average deviation of only 0.9 percent from the average value. This deviation is less than one-third of that obtained by simply assuming that the maximum will occur at an average equivalence ratio of 1.15. Bond energy calculations for 37 hydrocarbons similar to those presented in table IV had an average deviation of 1.6 percent.

For the equivalence-ratio data, linear relations were found between flame velocity and the logarithm of the equivalence ratio φ, where $\varphi<\varphi_{max}$. An interesting variation is the plot of flame velocity against the total bond dissociation energy of the fuel per unit volume of mixture in figure 4 for pentane, ethylene, and propyne mixtures with air. It may be seen that the correlation is linear for the lean mixtures and that the line extrapolates to the lean limit for flame propagation (where $U=0$) as determined in the 1-inch flame tube. For these data, determined by the tube method for three hydrocarbons, good estimates of the maximum flame velocities are obtained by reading from the curves at a total bond dissociation energy of 1.75 kilocalories per liter. This constant bond-energy value of 1.75 kilocalories per liter for this correlation does not equal the bond energy of the hydrocarbon concentration corresponding to the maximum flame velocity which was previously calculated to be 1.96 kilocalories per liter. Work with other flame-velocity data shows that both the position of the horizontal line and the slopes of the lines for specific hydrocarbons depend somewhat on the method of measurement of flame velocity.

TABLE III.—EMPIRICAL COEFFICIENTS FOR CALCULATING MAXIMUM FLAME VELOCITY FROM HYDROCARBON STRUCTURE (REF. 28)

Type C-H bond		Coefficient
Methane	K_A	35.2×10^{-19}
Primary	K_B	42.5
Secondary	K_C	47.5
Tertiary	K_D	45.4
Cyclohexyl	K_G	50.5
Alkene	K_E	80.7
Aromatic	K_H	84.3
Alkyne	K_F	223.9

TABLE IV.—BOND DISSOCIATION ENERGIES FOR C_4 AND C_6 HYDROCARBONS AT CONCENTRATION FOR MAXIMUM FLAME VELOCITY

Hydrocarbon	Equivalence ratio for maximum U, φ_{max}	Deviation of φ_{max} from average φ_{max}, percent	Dissociation energy of hydrocarbon, $\frac{kcal}{g\text{-mole}}$ (a)	Dissociation energy of mixture at φ_{max}, $\frac{kcal}{liter}$	Deviation from average, percent
Butane	1.09	5.5	1250	1.93	2.0
Hexane	1.16	0.9	1791	2.00	1.5
2-Methylpropane	1.11	3.6	1257	1.94	1.5
2, 2-Dimethylbutane	1.12	2.5	1821	1.97	0.0
Butene-1	1.17	1.7	1133	1.98	0.5
Hexene-1	1.16	0.9	1680	2.02	2.5
Isobutene	1.14	0.9	1147	1.97	0.0
2-Methylpentene-1	1.19	3.4	1603	1.99	1.0
Butyne-1	1.17	1.7	1016	1.95	1.0
Hexyne-1	1.21	5.0	1564	1.97	0.0
4-Methylpentyne	1.18	2.5	1574	1.95	1.0
Benzene	1.34	14.2	1305	1.96	0.5
Average	1.15	3.29	------	1.96	0.9

a Single-bond energies from ref. 29. Multiple-bond energies from ref. 30: 151.2 kcal/g-mole for C=C in olefins and cyclic compounds; 198.5 kcal/g-mole for C≡C bond.

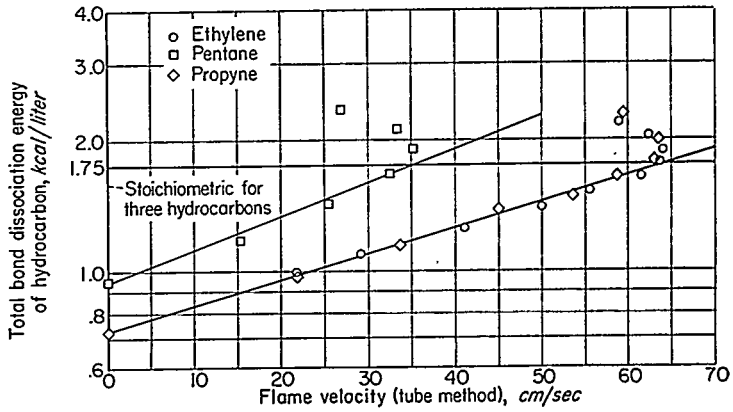


FIGURE 4.—Empirical correlation for equivalence-ratio data.

Empirical equations predicting the effect of initial mixture temperature on flame velocity with mean deviations of approximately 2 percent for the range from 200° to 615° K are (ref. 5):

For methane:

$$U=10+7.40\times10^{-5}T_0^{2.23}$$

For propane:

$$U=10+3.42\times10^{-4}T_0^{2.00}$$

For ethylene:

$$U=10+2.59\times10^{-3}T_0^{1.74}$$

Empirical relations were found which predict the effect of oxygen concentration (for the experimental range covered) and limited temperature (311°–422° K) on the flame velocity for the three hydrocarbons studied (ref 6):

For 2,2,4-trimethylpentane:

$$U=0.133\ T_0^{1.40}\ (\alpha-0.120)$$

For propane:

$$U=0.766\ T_0^{1.16}\ (\alpha-0.133)$$

For ethylene:

$$U=0.998\ T_0^{1.18}\ (\alpha-0.133)$$

The accuracy of prediction was about 3 percent for ethylene and 2,2,4-trimethylpentane and 6 percent for propane.

CONCLUDING REMARKS

The semitheoretical calculations of this paper are dependent on the assumption that thermal equilibrium is attained at the end of the combustion zone. Actual flame temperatures and product concentrations would differ from equilibrium values if (a) equilibrium is not attained, (b) any appreciable reaction takes place at the initial temperature, or (c) there is a large chain branching term affecting the radical distribution in and ahead of the flame zone. These calcu-

lations are also dependent on the inherent assumptions of the approximate theoretical equations and the methods used to calculate transport properties. Within these limitations, the results of the calculations may be generalized as follows:

1. The Semenov bimolecular equation (thermal mechanism), the Tanford-Pease square-root law (active-particle diffusion mechanism), and the Manson modification of the momentum-pressure-drop equation (including diffusion of active particles, but not chemical kinetics) will all predict relative changes in flame velocity caused by changes in hydrocarbon structure, initial temperature, equivalence ratio (limited range), or oxygen concentration. (The accuracies of the predictions are tabulated in this report.)

2. Low-temperature activation energies may be used in the Semenov equation to give good relative predictions of flame velocities for variations in initial temperature, equivalence ratio, and oxygen concentration. Only the bimolecular fuel-oxygen reaction is considered in this paper; other combinations such as fuel and hydrogen atoms should be investigated to determine whether the kinetics indicated for such other reactions are not more probable than for the fuel-oxygen case.

3. The average "specific rate constants" $\bar{k}_a$ obtained with the Tanford-Pease equation for molecular fuel—active particle reactions behave as Arrhenius rate constants only with the data on the effect of initial temperature, not with the equivalence-ratio or oxygen-concentration data. The relative predictions obtained by this equation are not very sensitive either to the temperature dependence assigned to the diffusion coefficients or to the recombination factor computed for hydrogen atoms; these factors do appreciably affect absolute predictions of flame velocity or, conversely, determinations of steric factors from experimental flame velocities. Regarding active particles considered, better results are generally obtained for hydrocarbon flames when H, OH, and O are considered rather than H alone; this is particularly true for studies of the effect of equivalence ratio.

4. For the equivalence-ratio and oxygen-concentration data, considerably better relative predictions are obtained from the Manson equation when the pressure drop across the flame front is considered to be due to H, OH, and O than when only H atoms are taken into account. Further thought should be given as to how this pressure drop should be computed, taking into account any net diffusional flow of any component between the flame front and the unburned gas.

5. The examples presented for the ethylene data show that an empirically determined rate constant or proportionality factor from equivalence-ratio data at atmospheric pressure and room temperature may predict the effect of initial temperature or oxygen concentration within approximately 20 percent by the Semenov or Tanford-Pease equation and within approximately 30 percent by the Manson equation.

6. For engineering applications, the effects of the parameters studied could be estimated just as satisfactorily, and more easily, by one or another of the empirical correlations indicated, as compared with the three semitheoretical equations considered. However, the use of the semitheoretical equations in some cases reduces the number of constants required.

LEWIS FLIGHT PROPULSION LABORATORY
NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS
CLEVELAND, OHIO, *January 2, 1953*

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